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ADHESIVE COMPOSITION FOR A HUMID MEDIUM, BASED ON BLOCK COPOLYMERS COMPRISING AT LEAST ONE HYDROPHILIC BLOCK

The present invention relates to the field of 5 block copolymers, in particular to the field of block copolymers containing at least one hydrophilic block, and more particularly to the use of such copolymers in adhesive formulations, especially adhesive formulations for use in a dry as well as in a moist medium.

10 The adhesive formulations of the invention can be used in a moist medium, particularly as regards any adhesion to the skin for a number of medical applications, (patches, prostheses) or paramedical applications (dressings) which have to stick even after 15 passage through water, as well as to the preparation of labels.

Current solutions in the field of adhesion in a moist medium are of the acrylic gum (hot melt or latex), vinyl polyacetate, polyvinylpyrrolidone, 20 silicone or polyurethane type. The majority of such products require chemical crosslinking of the hydrogen bond curing, UV curing, peroxide curing or wet curing type in the case of silanes. It should be noted that one of the key parameters in proposing an adhesive 25 formulation intended for cutaneous application is the fact that solvents which are not biocompatible cannot be used; all solutions involved in creating an adhesive are produced either by hot melt or by *in vivo* reaction.

A further solution which can be envisaged to avoid 30 using a solvent consists of using block copolymers the structure of which gives them the characteristics of crosslinked materials at the service temperature. In general, block copolymers used in the field of adhesive formulations are of the styrene/diene type. However, 35 styrenic and dienic monomers are hydrophobic and when they are used to bond substrates in a moist medium, the water prevents good contact of the substrate surfaces with the adhesive. Wholly acrylic copolymers have also

been envisaged (Mancinelli P. A., Seminar Proceeding (Pressure Sensitive Tape Council), 2-5 May 1989, 161-181), but the hydrophobic nature of acrylates and methacrylates does not allow adhesion in a moist
5 medium.

Thus, the invention seeks to overcome the problem of developing formulae for block copolymers that can be used in adhesive formulations which bond both in a dry medium and in a moist medium.

10 The Applicant has discovered that the solution to the problems mentioned above resides in the use in the adhesive formulations of a block copolymer having at least one strongly hydrophilic block and at least one hydrophobic or very slightly hydrophilic block.

15 The term "very slightly hydrophilic" as used by the Applicant means blocks with a water absorption capacity w_∞ , as defined below, of less than 20% and preferably less than 10%.

The hydrophilic block is rigid and constitutes the
20 minor phase dispersed in nanodomains (capsules, cylinders or lamellae), while the hydrophobic block is elastomeric in nature and constitutes the continuous phase.

25 The Applicant initially established that, for a block copolymer type adhesive, the continuous phase which allows adhesion is generally a hydrophobic phase as no truly hydrophilic and elastomeric monomers exist (with the exception of methoxyethyl acrylate, which the Applicant excluded from the investigations because of
30 its toxicity). For this reason, moist medium adhesion is rendered difficult. The Applicant has surprisingly realized that hydrophilic polymer domains nanodispersed in the hydrophobic matrix can make the material bond even in a moist medium.

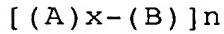
35 In a nanostructured material in which the hard phase is in the minority and hydrophilic, water penetrates the structure very rapidly and plasticizes the hydrophilic domains. The hydrophobic elastomer,

which absorbs on average 1% to 2% by weight of water, does not confine the water between the two surfaces to be bonded but transports it towards the hydrophilic domains which act like sponges. The nanostructuring 5 persists despite plasticization of said domains, which maintains the viscoelastic properties of the material and thus retains its adhesive properties.

As will be explained below, the Applicant has shown that in a moist medium, its block copolymers 10 endow adhesive formulations with very rapid adhesion, with high water permeability and with ease of use without post-curing.

In a first aspect, the invention concerns an adhesive composition for moist medium adhesion 15 comprising, as the binder, a block copolymer having at least one rigid hydrophilic block (B) constituting the minor phase dispersed in the form of nanodomains and at least one hydrophobic block (A) with an elastomeric nature having a water absorption capacity of less than 20 20%, constituting the continuous major phase.

The copolymers of the invention have the following general formula:



in which x is between 1 and 8, n is a whole number 25 in the range 1 to 3, A and B respectively represent from 50% to 99%, preferably from 65% to 95% by weight, and from 1% to 50%, preferably from 10% to 35% by weight of the total copolymer weight. The number average molar mass (M_n) of the copolymer is in the 30 range from 5000 g/mol to 300 000 g/mol with a polydispersity index in the range from 1.1 to 3.

In accordance with the invention, the adhesive force of the composition or formulation depends on the difference in water absorption capacity of each block, 35 hereinafter designated w_∞ , and is estimated as indicated below and expressed as a %.

Method for determining w_∞ :

A thin layer of a dry sample of polymer is prepared then exposed to an atmosphere with 98% humidity, thermostatted at 22°C. The water absorption is then measured using the equation:

5 $w(t) = \frac{m(t) - m^o}{m^o} \%$

where $m(t)$ designates the mass of the sample as a function of time, m^o the initial moist mass and w_∞ then corresponds to the plateau of $w(t)$ reached after a long period.

In the case of polydimethylacrylamide, the water absorption is 113% while that for butyl polyacrylate is 1.6%. The diffusion of water through a material follows Fick's law:

For $w < 0.6 w_\infty$, $\frac{w(t)}{w_\infty} = \frac{4}{e} * \left(\frac{D * t}{\pi}\right)^{1/2}$, in which e

designates the thickness of the sample. In the case of polydimethylacrylamide, for example, the diffusion D is $3.10^{-13}.s^{-1}$.

20 As claimed in the invention, the optimum in terms of adhesive force is reached with a ratio $w_\infty(B)/w_\infty(A)$ of more than 1, preferably more than 10 and more precisely more than 40.

In accordance with the preferred mode of the invention, $w_\infty(A)$ is less than 5% and $w_\infty(B)/w_\infty(A)$ is more than 20.

A has a glass transition temperature ($Tg(A)$) of less than 30°C and is thus qualified as a block with an elastomeric nature. In contrast, B must have a Tg ($Tg(B)$) of more than 50°C. Preferably, $Tg(A)$ is in the range from -120°C to 0°C, $Tg(B)$ is in the range from 20°C to 160°C.

The copolymers of the invention can be obtained using conventional polymerization techniques carried out in an organic or aqueous solution, by emulsion polymerization or by bulk polymerization, as described in the International Journal of Adhesion & Adhesives

22, 37-40 (2002). They are preferably prepared by controlled radical polymerization (CRP) in solution or in bulk.

Other techniques are possible but are more
5 sensitive to the reactive functions of the monomers such as amides (for example by anionic polymerization). The advantage of CRP is that it is highly tolerant as regards the choice of monomers and for this reason, the Applicant used this synthesis technique.

10 The preferred preparation mode of the invention is that described in French patent application FR-99 01998 of 18th February 1999, publication number FR-A-2 789 991.

A is obtained by polymerizing at least one monomer
15 selected from the group containing hydrophobic monomers such as acrylic esters, for example butyl acrylate or hexyl acrylate, conjugated dienes. Preferably, butyl acrylate is used.

B is obtained by polymerizing at least one monomer
20 selected from the group containing hydrophilic monomers such as acrylic acid, methacrylic acid, acrylamide, dimethylacrylamide, vinylpyrrolidone. It is preferably dimethylacrylamide. Monovalent salts of acrylic or methacrylic acids such as the sodium or lithium salts
25 are also included in these hydrophilic monomers.

A and B can respectively contain residues of hydrophilic and hydrophobic monomers provided that the ratio of their water absorption capacity remains within the range defined above.

30 Nanostructuring of the copolymer is the resultant of a set of parameters such as chemical nature and block length. Whatever the choice of A and B, it is vital that the nanostructuring is preserved. Considerations that allow the nanostructuring to be
35 preserved are known to the skilled person and reference can be made to the reference text: G Holden et al, in "Thermoplastic elastomers", 2nd edition, Carl Hanser Verlag, Munich, Vienna, New York, 1996.

The compositions of the invention also contain all of the additives necessary to shape them as well as the additives necessitated by the applications. The skilled person knows how to select these additives and 5 how to define the processing conditions as a function of the envisaged application.

In all of its implementations, the compositions of the invention do not require post curing after processing.

10 The adhesive formulations of the invention can be used in a moist medium, in particular as regards any adhesion to the skin for a number of medical applications (patches, prostheses...) or paramedical applications (dressings) which must adhere even after 15 passage through water, as well as in the field of labeling.

The following examples illustrate the invention without limiting its scope.

20 **Examples**

Examples 1 to 9 are in accordance with the invention. Examples 10 and 11 are comparative.

PDMA-*b*-PAbu (poly(*N,N*-dimethylacrylamide)-block-n-butyl polyacrylate) copolymers were synthesized by 25 starting from the PDMA block. PDMA was synthesized by controlled radical polymerization (CRP). The control agent was N-tert-butyl-1-diethylphosphono-2,2-dimethylpropyl nitroxide, hereinafter designated SG1.

30 **Purification of reagents**

Poly(*N,N*-dimethylacrylamide) was stored in a desiccator under vacuum or under nitrogen. The n-butyl acrylate was cryodistilled over calcium hydride and stored in a refrigerator in a burette with ground 35 graduations under nitrogen.

Azo-bis-isobutyronitrile (AIBN) was recrystallized from ether and vacuum dried prior to being stored in a refrigerator in a flask under nitrogen.

The SG1 (83% and 90%) was used as supplied.

The solvents for precipitation were of analytical grade and used without purification.

5 Synthesis

The calculated masses (see below) for the macro-initiator (PDMA) and SG1_{exc} were introduced into a Schlenk tube provided with a bar magnet. The Schlenk tube was connected to the burette, which latter was 10 placed under a slight over-pressure of nitrogen to add the desired volume of monomer. The reaction medium was homogenized well and underwent 3-4 vacuum (Schlenk tube immersed in liquid nitrogen)/nitrogen cycles to remove all traces of oxygen. The Schlenk tube was then 15 immersed in an oil bath at 110°C.

The polymer obtained was dissolved in THF, precipitated from a methanol/water = 2/1 mixture at 0°C and then filtered through a frit (no. 4, at 0°C). In the case in which a portion of the copolymer passed 20 through the frit, the filtrate was centrifuged (10 000 rpm, 10 min, ambient temperature).

The residue was oven dried at 40°C under vacuum (not exceeding 50°C!) for 2-3 days.

25 Calculation of masses

The calculated masses of PDMA and SG1 depended on the total mass m and on the envisaged number average molar mass M_n of the copolymer, as well as on the conversion. These three parameters had to be selected 30 initially (see paragraph above). The chains were "protected" by the SG1. However, to keep the polymolecularity indices as low as possible, addition of an excess of SG1 was recommended. Then the mass m_{b11} of the first block and the mass m_{SG1} of SG1 were 35 calculated as follows:

Mass of first block:

Universal formula:

$$m_{bl} = \frac{\overline{M}_{nbl} \times V_{mono_bl2+solv} \times d_{mono_bl2} \times conv.}{\overline{M}_{nblvisée} \times n_{radicaux}}$$

in which: m_{bl1} = mass of block 1
 \overline{M}_n = number average molar mass
5 $V_{mono_bl2+solv}$ = block monomer 2 volume
 plus solvent volume
 d_{mono_bl2} = density of block monomer
 2
10 $n_{radicaux}$ = number of radicals per
 initiator molecule
 conv. = degree of conversion
 ($n_{monomer\ t=0}/n_{monomer\ t=0}$)

Here:

$$m_{PDMA} = \frac{\overline{M}_{nPDMA} \times m_{Abu} \times conv.}{\overline{M}_{nAbuvisée}}$$

- 15 • Mass of excess SG1:

Preferably, the concentration ratios
 $[SG1_{exc}]/[(macro-)initiator] = 0.2-1.0$ are used.

Here:

$$m_{SG1} \approx 293 \times ("ratio") \times m_{PDMA} / \overline{M}_{nPDMA}$$

20 The characteristics of the products obtained are summarized in Table 1.

Application: practical results.

A/Preparation of adhesive formulations

The adhesives were prepared as follows:

- 25 • 450 μ l of a 15% solution of copolymer in dioxane were deposited on an anodized aluminum plate ($2.5 \times 2.5 \times 0.1$ cm). A tackifying or plasticizing resin could be added to the solution in proportions that are known to the skilled person.
- 30 • The solvent was evaporated off over two days at ambient temperature (in a Petri dish) before drying it completely in a vacuum oven at 50°C for two additional days.
- 35 The films obtained were $90 \pm 10 \mu\text{m}$ thick.

B/ Description of the method for measuring adhesion

The tack properties of the copolymers were measured on a dry and moist surface using the *probe 5 tack test*. It consisted of:

- a **compression step**: a probe was brought towards the adhesive until a nominal contact force F_c is attained;
- a **relaxation step**: the adhesive was allowed to relax for a contact time t_c at constant thickness;
- a **tensile step**: the probe was withdrawn at a constant velocity v .

The experiments were carried out using a tensile machine sold by the company Zwick. A motor produced the vertical displacement of the probe. This latter was connected to a 100 N force sensor fixed to a crossbeam. The force sensor and a position sensor provided us with access to the force and position of the crossbeam at any time (t). The experiments were carried out at ambient temperature, $F_c = 35$ N, $t_c = 100$ s and $v = 10$ mm/min.

The probe used was a cylinder with a planar surface (7 mm diameter) formed from stainless steel. For the moist surface measurements, the probe was immersed in a beaker filled with distilled water so that one drop covered its entire surface.

The tack curves represented only the portion relating to separation of the bond in the stress-strain coordinates. The stress σ was obtained by normalizing the force using the contact area. This latter was determined by measuring the area of the trace left by the probe on the adhesive, once the experiment was finished. The strain d was that of the probe.

The tack energy G corresponds to the integral of the curve in stress-strain coordinates and represents the energy that has to be provided to break the adhesive bond.

1. Dry medium adhesion measurement

The results are shown in Table 1.

A comparison of the samples prepared at 1 with a homopolymeric polybutyl acrylate (PABu) shows the importance of nanostructuring in obtaining the property of adhesion. A comparison with the formulation starting from Kraton (SBS) type triblock copolymer shows that in a dry medium, the diblock copolymers prepared at 1 are less adhesive than a triblock formulation.

2. Moist medium adhesion measurements:

The results are shown in Table 1.

A comparison shows that the formulations based on copolymers 2 or 3 bonded better than the reference formulation based on SBS.

Table 1: Characteristics of tested products and results obtained:

Test no	ADHESION RESULTS			Moist medium	
	Mn co-polymer	Poly-dispersity index	Dry medium		
			Modulus (G/cm ²)	Type	
1	83 000	1.20	120	Cohesive	
2	73 000	1.29	120	Cohesive	245
3	158 000	1.40	380	Adhesive	125
4	54 400		100	Cohesive	
5	63 000		100	Cohesive	
6	72 000		110	Cohesive	
7	94 000		180	Cohesive	
8	75 000		120	Cohesive	
9	85 000		135	Cohesive	
10: SBS			600	Adhesive	25
11: PABu	65 000	1.2	40		